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CALCULATION OF VISCOSITY IN MOLTEN SALTS (OXIDES)

by O. K. Sokolov

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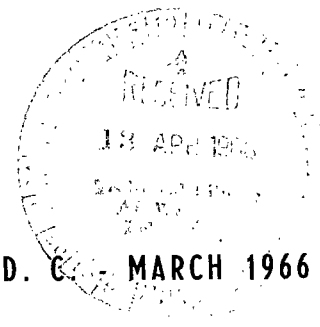

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CALCULATION OF VISCOSITY IN MOLTEN SALTS (OXIDES)

O. K. Sokolov

ABSTRACT

The author derives an equation based on Coulomb's law for calculating the viscosity of molten salts (oxides) in which there are two or fewer anions per cation. Viscosities calculated on the basis of this equation agree satisfactorily with experimental data. Tables are given showing viscosities calculated on the basis of this formula for several salts for which there are no empirical data.

The understanding of many pyrometallurgical processes is dependent /89* on a knowledge of the viscosity of melts, a subject on which available data are scarce. The author previously suggested (reference 1) that the viscosity of salts (oxides) might be evaluated qualitatively from their crystalline and chemical properties. However, qualitative evaluation is not enough. Therefore we propose an equation for calculating the viscosity of salts (oxides) at temperatures close to their melting points.

As is generally known, the viscosity of a liquid is defined as its capacity to resist the mutual displacement of its parts. For two layers of a liquid, having a contact area s and moved by a force F with velocities v_1 and v_2, the force necessary for maintaining a constant difference in velocities may be expressed as (reference 4)

$$F = \eta s \frac{v_1 - v_2}{x},$$

where x is the distance between layers measured perpendicular to the direction of motion, and η is viscosity.

*Numbers given in the margin indicate the pagination in the original foreign text.

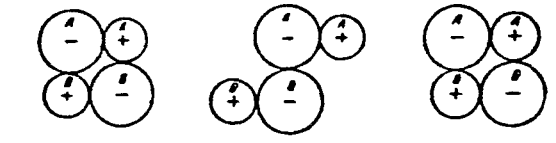
Let us examine the nature of viscosity in melts. Consider a microscopic quantity of the melt. Here the viscosity is determined by the resistance to displacement offered by one group of ions with respect to another identical group of ions corresponding to the short-range order of the crystal lattice structure of the salt (oxide). And since the melt as a whole is made up of a large number of such microscopic quantities, i.e., groups of ions which are not isolated but are united by mutual attraction, the viscosity of molten media is also determined by the ability of one group of ions to move with respect to another group. The viscosity in melts of salts (oxides) having more than two cations is determined by the capacity of a part of an ion group to move with respect to another part of the same group. We shall define a part of an ion group as one cation and the anions of the given salt (oxide) bound to this ion. In order to simplify the discussion in deriving the equation, it will be assumed below that a group of ions consists of one cation with a number of anions equal to the valence of this cation.

A further explanation is necessary for the factors which accelerate or retard this movement of ions, which depends on the force of interaction between ions of opposite sign. The resistance to motion between two groups of ions, and consequently the viscosity of the molten salt (oxide), increases with the strength of this interaction. The force of attraction F' between two ions of opposite sign is given by Coulomb's law /90

$$F = \frac{z_1 z_2 e^2}{d^2},$$

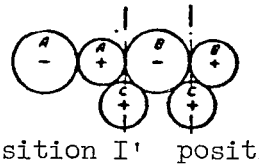
where z_1 and z_2 are the ion valences, e is the charge of the electron and d is the distance between the centers of the ions.

The figure shows that the force of interaction affects the motion of one group of ions with respect to another in position I. But the force calculated



position I position II position III

a



position I' position II'

b

Interaction between two groups of ions.

according to Coulomb's law is not identical to the force which opposes the motion of one group of ions with respect to another. In the case of univalent anions and cations (see figure) this latter force is twice as great as that calculated according to Coulomb's law, and for the case where the valence of the cation is higher, the force calculated according to Coulomb's law must be increased by a factor of (n + 1) where n is the number of anions bound to a single cation. In this case the effective force in position I is given by the equation

$$F_1 = \frac{z_1 z_2 e^2}{d^2}(n+1)$$

In position II, the force of interaction has no effect on the restraint of one group of ions with respect to another, but this force begins to operate in position III. However, in positions I' and II' the cation is acted on simultaneously by forces of mutual interaction and repulsion (see figure b) so that the force Φ' opposes the displacement of one group of ions with respect to the other on a path equal to $2r_a - r_c$ or, expressing r in terms of d, $3r_a - d$.

In position II, the repulsive interaction between like ions causes /91
mutual displacement which increases with the valence of the anions. Consequently, the viscosity of the melt may be expressed by the equation

$$\eta = \frac{z_k z_a e^2}{d^2 z_a}(3r_a - d)(n+1) \text{ or}$$

$$\eta = \frac{z_k e^2}{d^2}(3r_a - d)(n+1).$$

In order to use this equation for determining the absolute viscosities (in poises) of molten salts (oxides) close to their melting points, the coefficient k must be introduced, and the equation takes the final form

$$\eta = \frac{z_k e^2}{d^2}(3r_a - d)(n+1)k.$$

The coefficient k is expressed in sec/cm^3 and depends on the type of anion. We calculated k from experimental data, arriving at a value of 10 for chlorides and fluorides, and 10^4 for sulfides and oxides. The coefficient k may be calculated for salts with any anion if there are empirical data available on the viscosity of even one salt with the given anion.

The empirical data on the viscosities of several salts are given in table 1 together with the theoretical values calculated from the equation proposed in

TABLE 1. EXPERIMENTAL AND THEORETICAL VISCOSITY OF SEVERAL MOLTEN SALTS.

Salt	Melting point, °C	Temperature, °C	Viscosity, poises	
			Experimental value (ref. 4)	Theoretical value
LiCl	614	617	0.01810	0.0202
NaCl	800	816	0.01490	0.0152
AgCl	455	603	0.01606	0.0165
KCl	790	800	0.01080	0.0107
$MgCl_2$	718	808	0.04120	0.0585
$CaCl_2$	772	800	0.04940	0.0511
B_2O_3	847	850	170.0*	144.0
		900	118.0	

*O. A. Yesin and V. P. Gel'd Physical Chemistry of Pyrometallurgical Processes, Vol. II, p. 258, Metallurgizdat (Metallurgy Publishing House), 1954.

TABLE 2. VISCOSITY CALCULATED FROM THE FORMULA DERIVED IN THIS PAPER FOR SEVERAL HALIDES AT A TEMPERATURE SOMEWHAT HIGHER THAN THEIR MELTING POINTS.

Salt	Distance between the anion and cation in the crystal, Å (refs. 2 and 3)	Viscosity, poises	Salt	Distance between the anion and cation in the crystal, Å (refs. 2 and 3)	Viscosity, poises
LiCl	2.56	0.0202	AgF	2.46	0.0116
AgCl	2.77	0.0165	KF	2.67	0.0086
NaCl	2.81	0.0152	RbF	2.82	0.0068
KCl	3.14	0.0107	CsF	3.00	0.0051
RbCl	3.27	0.0094	BeF_2	1.57	0.1345
TlCl	3.32	0.0088	NiF_2	2.00	0.0677
CuCl	2.34	0.0269	CoF_2	2.00	0.0677
CsCl	3.56	0.0068	MgF_2	2.05	0.0640
$HgCl_2$	2.25	0.0867	FeF_2	2.12	0.0577
$MgCl_2$	2.59	0.0585	PdF_2	2.15	0.0552
$CaCl_2$	2.70	0.0511	CdF_2	2.34	0.0417
$SrCl_2$	3.02	0.0367	CuF_2	2.34	0.0417
$BaCl_2$	3.05	0.0335	CaF_2	2.36	0.0405
CuF	1.84	0.0294	HgF_2	2.40	0.0384
LiF	2.01	0.0226	SrF_2	2.50	0.0330
NaF	2.31	0.0145	PbF_2	2.57	0.0092
			BaF_2	2.68	0.0252

TABLE 3. VISCOSITY CALCULATED FROM THE FORMULA DERIVED IN THIS PAPER FOR SEVERAL SULFIDES AT A TEMPERATURE SOMEWHAT HIGHER THAN THEIR MELTING POINTS.

Sulfide	Distance between anion and cation in the crystal, Å (refs. 2 and 3)	Viscosity, poises	Sulfide	Distance between anion and cation in the crystal, Å	Viscosity, poises
Cu_2S	2.24	20.5	MnS	2.60	35.6
Li_2S	2.47	15.9	MgS	2.60	35.6
Na_2S	2.32	10.3	CaS	2.84	27.6
K_2S	3.20	6.8	PbS	2.95	24.1
Rb_2S	3.31	6.0	SnS	2.99	22.2
BeS	2.10	66.0	SrS	3.01	20.5
CuS	2.19	58.8	BaS	3.19	18.5
CoS	2.33	49.5	FeS_2	2.09	199.0
NiS	2.35	48.1	MoS_2	2.35	145.0
ZnS	2.35	48.1	TiS_2	2.42	134.0
FeS	2.45	42.1	WS_2	2.48	122.0
CdS	2.52	39.5	ZrS_2	2.58	111.5
HgS	2.53	38.7			

this paper. These data show satisfactory agreement. This indicates that the proposed equation may be used for calculating the viscosity of molten salts (oxides) which have two or fewer anions per cation. This is due to the assumption that the proposed equation cannot account for the force of interaction and the path along which this force is effective (between groups of ions) for salts (oxides) in which there are more than two anions per cation. /92

Viscosities calculated on the basis of the proposed equation for several chlorides, fluorides, sulfides and oxides for which there are no experimental data are given in tables 2, 3 and 4.

TABLE 4. VISCOSITY CALCULATED FROM THE FORMULA DERIVED IN THIS PAPER FOR SEVERAL OXIDES AT A TEMPERATURE SOMEWHAT HIGHER THAN THEIR MELTING POINTS.

Oxide	Distance between the anion and cation in the crystal, Å (refs. 1 and 3)	Viscosity, poises	Oxide	Distance between the anion and cation in the crystal, Å	Viscosity, poises
Cu_2O	1.84	21.60	Ga_2O_3	2.00	84.5
Li_2O	2.00	16.90	Mn_2O_3	2.01	83.0
Ag_2O	2.05	15.80	Fe_2O_3	2.06	77.3
Na_2O	2.40	9.35	Cr_2O_3	2.10	73.0
K_2O	2.70	5.20	In_2O_3	2.16	66.7
Rb_2O	2.92	4.25	Sb_2O_3	2.22	61.3
BeO	1.64	60.00	Tl_2O_3	2.26	57.3
ZnO	1.93	50.25	Y_2O_3	2.27	56.6
CuO	1.95	48.50	SiO_2	1.62	247.0
VO	2.04	42.25	VO_2	1.93	150.5
NiO	2.08	40.25	TiO_2	1.97	142.0
TiO	2.08	40.25	GrO_2	1.97	142.0
MgO	2.10	38.85	RuO_2	1.98	139.5
CoO	2.13	37.30	OsO_2	1.99	138.0
FeO	2.14	36.75	WO_2	2.00	135.0
MnO	2.20	33.60	MoO_2	2.00	135.0
PbO	2.20	33.60	NbO_2	2.01	132.5
CdO	2.35	26.85	PbO_2	2.16	107.0
CaO	2.40	25.10	ZrO_2	2.20	101.0
SrO	2.58	19.15	CeO_2	2.34	82.0
BaO	2.77	14.35	UO_2	2.37	78.0
B_2O_3	1.66	144.00	ThO_2	2.43	71.7
Al_2O_3	1.93	94.30			

Conclusions

1. An equation for the calculation of viscosity in molten salts (oxides) is presented.

2. Viscosities for several chlorides, fluorides, sulfides and oxides are calculated.

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